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## Modeling the fate of volatile organic compounds in wastewater treatment facilities; implementation of volatilization models in envirocad

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## **ABSTRACT**

### **MODELING THE FATE OF VOLATILE ORGANIC COMPOUNDS IN WASTEWATER TREATMENT FACILITIES; IMPLEMENTATION OF VOLATILIZATION MODELS IN ENVIROCAD**

**by  
Vinita Chhahira**

The 1990 Clean Air Act Amendments have identified wastewater treatment facilities as a major source of volatile organic compound (VOC) emissions. VOCs present in wastewater discharges affect the quality of receiving waters, while emissions to the air affect downwind populations. The primary mechanisms involved in VOC removal from a wastewater treatment facility are volatilization and stripping, biodegradation, and sorption to either suspended or biological solids. Although many models have been developed to predict the fate of VOCs in wastewater treatment facilities, no model completely predicts emissions for an entire wastewater treatment facility. The focus of this work is to incorporate appropriate models for volatilization into an environmental computer-aided design tool called EnviroCAD, which simulates several unit operations used for wastewater treatment. An example and sensitivity analysis illustrate the feasibility of using process simulators, such as EnviroCAD, to predict the fate of VOCs in wastewater treatment facilities under several operating conditions, as well as determine whether or not the facility is in violation of any environmental regulations regarding VOC emissions.

**MODELING THE FATE OF VOLATILE ORGANIC COMPOUNDS IN  
WASTEWATER TREATMENT FACILITIES; IMPLEMENTATION OF  
VOLATILIZATION MODELS IN ENVIROCAD**

by  
**Vinita Chhahira**

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## LIST OF SYMBOLS

$a$	= Surface area to volume ratio of the tank ( $m^{-1}$ )
$A$	= Surface area of the tank ( $m^2$ )
$A_a$	= Reactor surface area divided by the number of aerators ( $m^2$ )
$C'$	= Oxygen saturation concentration at a specific temperature and barometric pressure ( $mg/m^3$ )
$C^*$	= VOC concentration in the liquid phase that would be in equilibrium with the VOC concentration in the bulk gas phase ( $g/m^3$ )
$C_g$	= VOC concentration in bulk gas phase ( $g/m^3$ )
$C_{g,in}$	= Initial VOC concentration in the air circulating through a trickling filter ( $g/m^3$ )
$C_{g,out}$	= Final VOC concentration in the air circulating through a trickling filter ( $g/m^3$ )
$C_l$	= VOC concentration in the bulk liquid phase ( $g/m^3$ )
$C_{l,in}$	= Influent VOC concentration in the wastewater ( $g/m^3$ )
$C_{l,out}$	= Effluent VOC concentration in the wastewater ( $g/m^3$ )
$d$	= Depth of the liquid inlet flow into the junction box (cm)
$d_e$	= Effective diameter of the tank (m)
$D_a$	= Diffusivity of the VOC in air ( $cm^2/s$ )
$D_e$	= Diffusivity of ether in water ( $cm^2/s$ )
$D_i$	= Diffusivity of compound i in water ( $m^2/s$ )
$D_{O_2}$	= Liquid diffusion coefficient for oxygen ( $m^2/s$ )
$D_{VOC}$	= Liquid diffusion coefficient for a VOC ( $m^2/s$ )
$D_w$	= Diffusivity of the VOC in water ( $cm^2/s$ )
$f_{oc}$	= Fraction of organic carbon in solids
$F/D$	= Fetch-to-depth ratio
$H_c$	= Dimensionless Henry's constant

## LIST OF SYMBOLS (Continued)

$k$	= Apparent first order biodegradation rate constant ( $\text{m}^3/\text{g s}$ ) = $\frac{\mu_m}{YK_s}$
$k_g$	= Gas phase transfer coefficient ( $\text{m/s}$ )
$k_l$	= Liquid phase transfer coefficient ( $\text{m/s}$ )
$k_{l,\text{O}_2}$	= Liquid phase transfer coefficient for oxygen ( $\text{m/s}$ )
$k_{l,\text{VOC}}$	= Liquid phase transfer coefficient for a VOC ( $\text{m/s}$ )
$k_o$	= System-specific oxygen transfer coefficient ( $\text{s}^{-1}$ )
$k_p$	= Solid/liquid partition coefficient ( $\text{m}^3/\text{g VSS}$ )
$k_p'$	= Freundlich adsorption parameter
$K_L$	= Overall mass transfer coefficient ( $\text{m/s}$ )
$(K_L a)_{\text{O}_2}$	= Overall mass transfer rate constant for dissolved oxygen ( $\text{s}^{-1}$ )
$(K_L a)_{\text{VOC}}$	= Overall mass transfer rate constant for a VOC ( $\text{s}^{-1}$ )
$K_{ow}$	= Octanol/water partition coefficient
$K_s$	= Half-saturation coefficient ( $\text{g/m}^3$ )
$n$	= Empirical constant
$N_c$	= Oxygen transfer rate per surface aerator in clean water under standard conditions ( $20^\circ\text{C}$ and $760\text{ mm Hg}$ ) ( $\text{kg O}_2/\text{KW h}$ )
$P$	= Brake power per aerator ( $\text{KW}$ )
$q$	= Compound sorption density ( $\text{g/g VSS}$ )
$Q$	= Wastewater flowrate into the tank ( $\text{m}^3/\text{s}$ )
$Q_e$	= Effluent flowrate ( $\text{m}^3/\text{s}$ )
$Q_g$	= Aeration rate ( $\text{m}^3/\text{s}$ )
$Q_w$	= Sludge flowrate ( $\text{m}^3/\text{s}$ )
$R_{\text{bio}}$	= Rate of compound removal by biodegradation ( $\text{g/s}$ )

## LIST OF SYMBOLS (Continued)

$R_{\text{sor}}$	= Rate of compound removal by sorption (g/s)
$R_{\text{vol}}$	= Rate of compound removal by volatilization (g/s)
$S$	= Concentration of the compound in the tank ( $\text{g/m}^3$ )
$Sc_G$	= Schmidt number of the VOC in the gas phase
$Sc_L$	= Schmidt number of the VOC in the liquid phase
$S_{\text{in}}$	= Concentration of the compound in the influent stream ( $\text{g/m}^3$ )
$t$	= Time (s)
$T$	= Absolute temperature (K)
$U$	= Wind velocity (m/s)
$U_{10}$	= Wind velocity at ten meters above the liquid surface (m/s)
$v$	= Waste velocity (cm/s)
$V_m$	= Molar volume ( $\text{cm}^3/\text{mol}$ )
$V$	= Volume of the tank ( $\text{m}^3$ )
$x$	= Association parameter for water = 2.26
$X$	= Concentration of biomass (g VSS/ $\text{m}^3$ )
$Y$	= Cell yield coefficient
$\alpha$	= Transfer coefficient ratio between wastewater and clean water
$\eta$	= Viscosity of water (cp)
$\mu_G$	= Viscosity of air (g/cm s)
$\mu_L$	= Viscosity of water (g/cm s)
$\mu_m$	= Maximum microbial growth rate ( $\text{s}^{-1}$ )
$\rho_G$	= Density of air ( $\text{g/cm}^3$ )
$\rho_L$	= Density of water ( $\text{g/cm}^3$ )

## LIST OF SYMBOLS (Continued)

$\psi$	= Dimensionless transfer coefficient proportionality constant for individual VOCs
$\psi_M$	= Modified dimensionless transfer coefficient proportionality constant for individual VOCs



## CHAPTER 1

### INTRODUCTION

Volatile organic compounds (VOCs) are chemical substances that are photochemically reactive. The United States Environmental Protection Agency (USEPA or EPA) further defines VOCs as organic chemicals with vapor pressures of 0.1 mm Hg or greater at standard conditions (20 °C and 760 mm Hg) (Mukhopadhyay and Moretti, 1993). VOCs photochemically react with nitrogen oxides and other airborne chemicals to form ozone and subsequently smog, which can cause haze, damage to plant and animal life, eye irritation, and respiratory problems in humans. Some VOCs, known as chlorofluorocarbons or CFCs, deplete ozone from the stratosphere. As a result, plant and animal life are left unprotected from high-energy solar radiation. Some VOCs are also known to be carcinogenic.

#### 1.1 Industrial Sources of VOC Emissions

Although VOCs are emitted in large quantities by mobile, commercial, and residential sources, a significant amount of emissions can also occur from industrial processes. VOC emissions from industry are typically categorized as follows: storage and handling emissions, process emissions, fugitive emissions, and secondary emissions. Storage and handling emissions depend on the construction and size of storage tanks, the vapor pressure of stored organic chemicals, and the ambient conditions at the particular tank's location (Chadha and Parmele, 1993). Working and breathing losses are also considered a part of this category. Handling losses also occur as a result of the transfer or loading and unloading of volatile organic chemicals from railcars and tank trucks. Process emissions occur from process reactor stacks and vents, recovery and control

equipment (absorbers, scrubbers, and carbon adsorption systems, etc.), and separation and purification equipment (Chadha and Parmele, 1993). Leaks from compressors, pumps, valves, flanges, open-ended lines, seals, and connections are classified as fugitive emissions (Corbitt, 1990). Fugitive emissions can occur from plant sources such as storage tanks and process operations as well (Chadha and Parmele, 1993). Secondary emissions, on the other hand, usually occur from wastewater collection and treatment systems, such as trenches, sumps, surface impoundments, and aeration basins (EPA, 1994).

Until recently, secondary emissions from wastewater treatment facilities were not regulated by federal, state, and local agencies. However, with the 1990 Clean Air Act Amendments, wastewater treatment facilities have been designated as a major source of VOC emissions and, as a result, are now being pressured to assess the fate of VOCs during each step of their treatment processes. They must also take appropriate measures to manage the release of VOCs from their facilities, using either wastewater treatment or emissions control methods or waste minimization techniques. However, before any of these technologies can be implemented, the mechanisms by which VOCs are removed and their rate of removal must be determined.

## **1.2 Mechanisms for VOC Removal in Wastewater Treatment Facilities**

VOC removal mechanisms are generally defined as methods by which a VOC is transported from or transformed in, for example, a chemical, pharmaceutical, or treatment process. The mechanisms of VOC removal involved in a typical wastewater treatment facility (see Appendix A) are the following: volatilization and stripping, biodegradation, sorption to solids, and pass-through. Organic compounds generally enter the air through volatilization if they have a relatively high Henry's constant or if treatment tanks are aerated. Biodegradation involves the partial or complete destruction

of a compound by aerobic organisms, and sorption involves the partitioning of organic compounds from the wastewater to the solids present in the wastewater stream. Volatile compounds generated as a result of chlorination or as byproducts of the biodegradation process are also included in these mechanisms. Compounds not affected by volatilization, biodegradation, and sorption are passed through the system, appear in the effluent, and are discharged into the environment. The environmental impact of each of the mechanisms mentioned above is provided in Table 1.

**Table 1** Environmental Impact of VOCs Removed from Wastewater Treatment Facilities (Levin and Gealt, 1993).

Removal Mechanism	Environmental Impact
Volatilization	Release of VOCs into the atmosphere; human exposure to carcinogens; contributes to ozone layer degradation
Biodegradation	None
Sorption	Toxic compounds carried with sludge to landfills; may result in groundwater contamination which can threaten drinking water supplies
Pass-through	Release of toxic compounds into surface waters (rivers, lakes, oceans); can contaminate drinking water sources and injure local ecosystems

### 1.3 Estimating VOC Emissions from Wastewater Treatment Facilities

Emissions of volatile organic compounds can be estimated by several techniques including gas phase and liquid phase measurements, mass balances, emission factors, and modeling.

#### 1.3.1 Measurements

One way to estimate the amount of VOCs entering the atmosphere is by taking either gas phase or liquid phase measurements. Volatilization to the air from large open surfaces can be measured in two ways: direct measurement and indirect measurement. Direct measurements are conducted in a surface isolation flux chamber, which uses an

enclosure device to sample gaseous emissions from a surface area (Freeman, 1989). The values from each measurement are then multiplied by the represented surface area to obtain the total surface emissions. Indirect measurements involve dispersion modeling to calculate fugitive emissions from area sources (Card and Desing, 1994). Liquid phase measurements can be made by sampling the wastewater at each step of the treatment process to determine the total amount of VOCs removed. In general, measurements of VOC emissions are fairly complex and very expensive.

### **1.3.2 Mass Balances**

General mass balances performed around wastewater treatment units are based upon the difference in the VOC mass loading in the influent and effluent streams. All unaccountable mass is assumed to be lost to the air through volatilization. Therefore, VOC emissions are generally overestimated since biodegradation and sorption to solids are not considered. Another disadvantage of a conservative mass balance like this is that the primary source of VOC emissions is not indicated unless data points are taken at each step of the treatment process.

### **1.3.3 Emission Factors**

Emission factors are also used to estimate organic emissions. Emission factors were developed by the Bay Area Air Toxics (BAAT) group and the Pooled Emissions Estimation Program (PEEP). BAAT emission factors are based on literature data related to the fate of VOCs in industrial and municipal wastewater treatment plants; PEEP emission factors were developed from samples of liquid and gas streams from similar processes at twenty publicly-owned treatment works (POTWs) in California (Card and Desing, 1994).

An emission factor is the average value of the ratio of the amount of a compound released to the air to the total quantity of the compound entering a unit process (Leong et al., 1992). Once the emission factor is known, the rate of a compound's release to the air can be calculated as follows:

$$\text{Emission Rate} = \text{Mass Loading Rate} \times \text{Emission Factor} \quad (1)$$

Even though the emission factor approach is simple and provides reasonable values, the primary mechanism by which VOCs are removed cannot be determined (Melcer, 1994). Also, this approach does not consider site-specific designs or differences in process variables between similar unit processes at different treatment plants (Mayer et al., 1994).

#### **1.3.4 Modeling**

Modeling the fate of VOCs requires a mathematical analysis of each of the VOC removal mechanisms in wastewater treatment plants. Modeling also involves rigorous mass balances which use rate expressions and equilibrium and mass transfer correlations to determine the extent of VOC removal.

In recent years, process modeling through computer simulation has become an extremely useful tool in designing and optimizing physical, chemical, and biological wastewater treatment processes. Modeling facilitates process development by identifying problems, as well as opportunities, during the early stages of design. Modeling can also reduce the cost of a new process by allowing engineers to analyze and refine processes, evaluate alternative operation strategies, and determine operability problems due to equipment malfunction (Glasscock and Hale, 1994). Limitations to modeling include the lack of reliable input data (such as thermodynamic or kinetic data),

the large number of process variables, and the nonlinear interactions among different variables within a process (Glasscock and Hale, 1994). Despite these disadvantages, there is a growing need for more realistic process simulation tools in order to maintain efficient plant operation and test alternate strategies for waste minimization.

#### **1.4 Predicting the Fate of VOCs with EnviroCAD**

The focus of this thesis is to study and evaluate different volatilization models used to estimate VOC emissions and, subsequently, incorporate them into an environmental computer-aided design tool called EnviroCAD (Petrides et al., 1994). EnviroCAD, currently under development at the New Jersey Institute of Technology, simulates several unit operations used for waste recovery, treatment, and disposal. Biodegradation models have already been implemented into EnviroCAD prior to this work; sorption to solids is not considered since it is an insignificant VOC removal mechanism.

The example and sensitivity analysis presented in this thesis demonstrate the feasibility of using models to predict the fate of VOCs in wastewater treatment facilities under several operating conditions. The implementation of these models into simulators, such as EnviroCAD, greatly simplifies the assessment of the total environmental impact of wastewater treatment facilities.

## CHAPTER 2

### VOC REMOVAL IN WASTEWATER TREATMENT FACILITIES

As mentioned previously, VOC removal in wastewater treatment plants occurs due to the following mechanisms: volatilization, biodegradation, and sorption. The next three sections describe each of these mechanisms in more detail and provide the equilibrium and mass transfer correlations used for each removal mechanism. The last section describes the general approach used in estimating VOC removal from wastewater treatment operations.

#### 2.1 Volatilization

The release of VOCs to the atmosphere can occur as a result of volatilization across open surfaces (natural volatilization), volatilization induced by mechanical surface aeration, and stripping by diffused (or bubble) aeration. The rate of mass transfer across the air-wastewater interface is written as follows:

$$R_{vol} = - K_L (C_l - C^*) A \quad (2)$$

or,

$$R_{vol} = - K_L a (C_l - C^*) V \quad (3)$$

where	$R_{vol}$ (g/s)	= rate of compound removal by volatilization
	$K_L$ (m/s)	= overall mass transfer coefficient
	$a$ ( $m^{-1}$ )	= surface area to volume ratio of the tank

$C_l$ (g/m <sup>3</sup> )	= VOC concentration in bulk liquid phase
$C^*$ (g/m <sup>3</sup> )	= VOC concentration in the bulk liquid phase that would be in equilibrium with the VOC concentration in the bulk gas phase
$A$ (m <sup>2</sup> )	= surface area of the tank
$V$ (m <sup>3</sup> )	= volume of the tank

and

$$C^* = \frac{C_g}{H_c} \quad (4)$$

where  $C_g$  is the VOC concentration in bulk gas phase in (g/m<sup>3</sup>) and  $H_c$  is the dimensionless Henry's constant.

$K_L$  (or  $K_L a$ ) is described by the two-film theory and is therefore dependent upon both the gas phase and liquid phase resistances.

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{H_c k_g} \quad (5)$$

$k_l$  and  $k_g$  are the liquid phase and gas phase transfer coefficients in (m/s), respectively. For highly volatile compounds ( $H_c > 0.2$ ), the gas phase resistance is negligible, and  $K_L = k_l$ . When  $H_c < 0.2$ , the gas phase resistance cannot be neglected, and the overall mass transfer coefficient must be determined. See Table 2 to compare the relative volatility of several common VOCs.

As mentioned above, if the gas phase resistance is neglected, then  $K_L = k_l$ .  $k_l$  is often calculated by the following equation (Govind et al., 1991):

$$k_{l,VOC} = \psi k_{l,O_2} \alpha \quad (6)$$



**Table 2** Dimensionless Henry's Constants for 10 VOCs at 20 °C. Adapted from Metcalf and Eddy (1991).

Compound	H <sub>c</sub>
Benzene	0.228
Chlorobenzene	0.154
1,2-dichloroethane	0.047
o-dichlorobenzene	0.071
Ethylbenzene	0.351
1,1,2,2-tetrachloroethane	0.017
Tetrachloroethylene	1.185
Toluene	0.268
1,1,1-trichloroethane	0.150
Trichloroethylene	0.487

where  $k_{l,VOC}$  and  $k_{l,O_2}$  are the liquid phase transfer coefficients for a VOC and oxygen in (m/s), respectively.  $\alpha$  is the transfer coefficient ratio between wastewater and clean water and its value increases as the degree of wastewater treatment increases.  $\alpha$  is given by the following equation:

$$\alpha = \frac{K_L a \text{ in wastewater}}{K_L a \text{ in clean water}} \quad (7)$$

where  $K_L a$  represents the overall mass transfer coefficient during oxygen transfer observed in either wastewater and clean water in ( $s^{-1}$ ). Values of  $\alpha$  for oxygen represent liquid film resistances only and should be used when VOCs are liquid film limited (Mihelcic et al., 1993).

$\psi$  is the dimensionless transfer coefficient proportionality constant for individual VOCs (Corsi and Card, 1991). Although  $\psi$  has been found to be approximately 0.6 for most volatile compounds in well-mixed systems, it can also be calculated by the following equation:

$$\psi = \left\{ \frac{D_{\text{VOC}}}{D_{\text{O}_2}} \right\}^n \quad (8)$$

where  $D_{\text{VOC}}$  and  $D_{\text{O}_2}$  are the liquid diffusion coefficients for a VOC and oxygen in ( $\text{m}^2/\text{s}$ ), respectively. The exponent  $n$  varies from 0.5 for penetration and surface renewal theories to 1.0 for two-film theory (Corsi and Card, 1991) and is typically 0.5 to 0.6 (Mihelcic et al., 1993). Diffusion coefficients, or diffusivities, of compounds in water can be approximated by the Wilke-Chang equation (Reid et al., 1987):

$$D_i = \frac{\{7.4 \times 10^{-8} (18x)^{0.5} T\}}{\eta V_m^{0.6}} \quad (9)$$

where	$D_i$ ( $\text{cm}^2/\text{s}$ )	= diffusivity of compound $i$ in water
	$x$	= association parameter for water = 2.26
	$T$ (K)	= absolute temperature
	$\eta$ (cp)	= viscosity of water
	$V_m$ ( $\text{cm}^3/\text{mol}$ )	= molar volume

$k_{\text{L},\text{O}_2}$  is given by several equations depending on the type of volatilization. For example, for systems with mechanical surface aeration, the following equation can be used to estimate  $k_{\text{L},\text{O}_2}$  (Corsi and Card, 1991):

$$k_{\text{L},\text{O}_2} = \frac{N_c P}{3600 A_a C} \quad (10)$$

where  $N_c$  is the oxygen transfer rate per surface aerator in clean water under standard conditions in ( $\text{kg O}_2/\text{KW h}$ ). Usually, the value of  $N_c$  is supplied by the manufacturers of the aerated unit (Corbitt, 1990).  $P$  is the brake power per aerator in (KW),  $A_a$  is the

reactor surface area divided by the number of aerators ( $\text{m}^2$ ), and  $C'$  is the oxygen saturation concentration in ( $\text{mg}/\text{m}^3$ ) at a specific temperature and barometric pressure.

### 2.1.1 Volatilization Across Open Surfaces

For wastewater treatment units that are open to the atmosphere, the accumulation of VOCs in the gas phase is negligible. Thus,  $C_g$  and therefore  $C^*$  are small, and  $K_L = k_l$ . The rate of compound removal by volatilization then becomes

$$R_{\text{vol}} = -k_l C_l A \quad (11)$$

This equation, however, overestimates emissions for covered processes or rising air bubbles that accumulate VOCs in the gas phase. In these cases, the overall mass transfer coefficient must be estimated in order to determine the VOC emissions rate.

### 2.1.2 Volatilization Induced by Mechanical Surface Aeration

In mechanical surface aeration systems, emissions occur due to the turbulent portion of the surface, airborne wastewater droplets, or mass transfer to entrained air bubbles. Equation 11 applies assuming that mass transfer to entrained air bubbles is negligible. If  $H_C < 0.2$ , however, gas phase resistance is important and the overall mass transfer coefficient must be used in order to estimate VOC emissions.

### 2.1.3 Stripping by Diffused Aeration

In diffused or bubble aeration, the gas phase concentration of the VOC is not assumed to be zero. In addition, if it is assumed that air bubbles rising to the top of the tank become saturated with a VOC during transport through the wastewater (Corsi and Card, 1991), the emissions rate is written as

$$R_{vol} = - Q_g H_c C_l \quad (12)$$

where  $Q_g$  is the aeration rate in ( $m^3/s$ ). If the rising bubbles are assumed to reach partial saturation, the rate is modified with a fractional saturation term (Corsi and Card, 1991):

$$R_{vol} = - Q_g H_c C_l \left\{ 1 - \exp \left( - \frac{\psi k_o V}{H_c Q_g} \right) \right\} \quad (13)$$

where  $k_o$ , which also equals  $k_{l,O_2}a$ , is the system-specific oxygen transfer coefficient in ( $s^{-1}$ ).

## 2.2 Biodegradation

Biodegradation involves the biochemical oxidation of an organic substance resulting from the complex action of living organisms (Freeman, 1989). Biodegradation is an important removal mechanism in activated sludge systems (Govind et al., 1991) and other biological treatment systems. The relative biodegradability of common VOCs is shown in Table 3.

**Table 3** Relative Biodegradability of VOCs. Adapted from Bohn (1992).

Rapidly Degradable VOCs	Slowly Degradable VOCs	Very Slowly Degradable VOCs
Alcohols Aldehydes Ketones Ethers Esters Organic Acids Amines Thiols Other molecules containing O, N, or S functional groups	Hydrocarbons Phenols Methylene Chloride	Halogenated Hydrocarbons Polyaromatic Hydrocarbons CS <sub>2</sub>

Biodegradation is usually modeled using Monod kinetics (Melcer, 1994):

$$R_{\text{bio}} = - \frac{\mu_m SXV}{Y(K_s + S)} \quad (14)$$

where	$R_{\text{bio}}$ (g/s)	= rate of compound removal by biodegradation
	$V$ (m <sup>3</sup> )	= volume of the tank
	$\mu_m$ (s <sup>-1</sup> )	= maximum microbial growth rate
	$S$ (g/m <sup>3</sup> )	= concentration of the compound
	$X$ (g/m <sup>3</sup> )	= concentration of biomass
	$K_s$ (g/m <sup>3</sup> )	= half-saturation coefficient
	$Y$	= cell yield coefficient

If the substrate concentration  $S$  is assumed to be significantly less than  $K_s$ , i.e., VOCs are present in the influent at low concentrations (which is the case for VOCs in most wastewaters), then Equation 14 can be rewritten as

$$R_{\text{bio}} = - \frac{\mu_m SXV}{YK_s} = - kSXV \quad (15)$$

where  $k$ , or  $\frac{\mu_m}{YK_s}$ , is the apparent first order biodegradation rate constant in (m<sup>3</sup>/g s).

Another assumption is that parameters other than the substrate concentration (nutrients and vitamins, for example) that may limit biodegradation are not considered (Govind et al., 1991). Also, inhibition effects on enzyme-catalyzed reactions and biodegradation due to cometabolism are ignored. Cometabolism refers to situations in which a chemical is metabolized but does not serve as a source of nutrients to the biological organisms (Freeman, 1989).

There are, however, limitations to the biodegradation model. First of all, there is a lack of experimentally determined biodegradation constants for VOCs (Govind et al., 1991). Published values for the rate coefficient vary by up to three orders of magnitude and have been shown to vary according to the degree of biomass acclimation (Melcer, 1994). In order to alleviate this problem, Govind et al. (1991) use a group contribution method in order to estimate the biodegradation rate constant. The best solution, however, is to use site-specific data.

Another problem involves the interpretation of  $X$ . Most models use either the total or a fraction of the volatile suspended solids (VSS) to describe the active biomass; all models assume acclimated biomass (Melcer, 1994). Others interpret  $X$  as a large fraction of the total biomass that would degrade VOCs by secondary utilization, a mechanism that enables the rapid biodegradation of individual trace-level compounds, even when they are present in very low concentrations (Namkung and Rittmann, 1987).

### 2.3 Sorption

Sorption, or adsorption, is a process by which soluble substances that are in solution are collected on a suitable interface. In primary systems of a wastewater treatment facility, VOCs are sorbed onto suspended solids, while in secondary systems, they are sorbed onto biomass. These losses, however, are small when compared to volatilization and biodegradation.

The removal rate of a compound by sorption onto biomass is given by

$$R_{\text{SOR}} = -Q_w X q \quad (16)$$

where  $R_{\text{SOR}}$  (g/s) = rate of compound removal by sorption  
 $Q_w$  (m<sup>3</sup>/s) = waste sludge flowrate

$X$  (g VSS/m<sup>3</sup>) = concentration of biomass

$q$  (g/g VSS) = compound sorption density

The compound sorption density, or amount of compound sorbed per unit weight of biomass, is given by

$$q = k_p S \quad (17)$$

where  $k_p$  is the solid/liquid partition coefficient in (m<sup>3</sup>/g VSS) and  $S$  is the concentration of the compound in (g/m<sup>3</sup>). Equation 17 represents a linear adsorption isotherm. Freundlich isotherms can also be used to model sorption to solids, where

$$q = k_p' S^{1/n} \quad (18)$$

$n$  is an empirical constant, which has been shown to be close to unity, proving that linear isotherms can be used to model removal by sorption.  $k_p'$  is the Freundlich adsorption parameter, which is dependent upon the octanol/water partition coefficient,  $K_{ow}$ .  $k_p'$  can be given by the following equation:

$$\log k_p' = 1.14 + 0.58 \log K_{ow} \quad (19)$$

The partition coefficient,  $k_p$ , used in linear isotherms, also depends upon  $K_{ow}$ . For hydrophobic pollutants (Karickhoff et al., 1979),

$$k_p = (6.3 \times 10^{-7}) f_{oc} K_{ow} \quad (20)$$

where  $f_{oc}$  is the fraction of organic carbon in solids. According to Metcalf and Eddy (1991),  $f_{oc}$  equals 0.531 when the biological cells are represented by  $C_5H_7O_2N$ . Therefore,  $k_p = (3.345 \times 10^{-7}) K_{ow}$ , and

$$R_{sor} = - (3.345 \times 10^{-7}) Q_w X K_{ow} S \quad (21)$$

Usually, the logarithm ( $\log_{10}$ ) of  $K_{ow}$  is found in the literature. Values of  $\log_{10} K_{ow}$  for some common VOCs are given in Table 4 below.

**Table 4**  $\log_{10} K_{ow}$  for 10 VOCs at 20 °C. Adapted from Metcalf and Eddy (1991).

Compound	$\log_{10} K_{ow}$
Benzene	2.12
Chlorobenzene	2.18
1,2-dichloroethane	1.45
o-dichlorobenzene	3.40
Ethylbenzene	3.13
1,1,2,2-tetrachloroethane	2.39
Tetrachloroethylene	2.53
Toluene	2.21
1,1,1-trichloroethane	2.17
Trichloroethylene	2.42

## 2.4 The General Fate Model

The general fate model uses the equations described in the previous sections to determine the removal of VOCs by volatilization, biodegradation, and/or sorption. Input to the model usually consists of influent VOC concentrations, VOC properties, wastewater flowrate, and process-specific design or operating parameters. A general mass balance for one component is usually written on a perfectly stirred reactor, and the balance is solved in order to find the effluent concentration of that particular component.



Once the effluent concentration is known, the rates of each removal mechanism can be found.

The general mass balance is written on a contaminant as follows:

$$\text{Accumulation} = \text{In} - \text{Out} + \left[ \begin{array}{c} \text{Rate of} \\ \text{Volatilization} \end{array} \right] + \left[ \begin{array}{c} \text{Rate of} \\ \text{Biodegradation} \end{array} \right] + \left[ \begin{array}{c} \text{Rate of} \\ \text{Sorption} \end{array} \right] \quad (22)$$

For a clarifier or aeration tank,

$$V \frac{dS}{dt} = QS_{in} - Q_e S - Q_w S + R_{vol} + R_{bio} + R_{sor} \quad (23)$$

where	$V \text{ (m}^3\text{)}$	= volume of the tank
	$S \text{ (g/m}^3\text{)}$	= concentration of the compound in the tank
	$t \text{ (s)}$	= time
	$Q \text{ (m}^3\text{/s)}$	= wastewater flowrate into tank
	$S_{in} \text{ (g/m}^3\text{)}$	= concentration of the compound in the influent stream
	$Q_e \text{ (m}^3\text{/s)}$	= effluent flowrate
	$Q_w \text{ (m}^3\text{/s)}$	= sludge flowrate
	$R_{vol} \text{ (g/s)}$	= rate of compound removal by volatilization
	$R_{bio} \text{ (g/s)}$	= rate of compound removal by biodegradation
	$R_{sor} \text{ (g/s)}$	= rate of compound removal by sorption

Assuming steady-state conditions and that the sum of the effluent flowrate and the sludge flowrate equals the influent wastewater flowrate, Equation 23 is reduced to

$$0 = Q (S_{in} - S) + R_{vol} + R_{bio} + R_{sor} \quad (24)$$

For a diffused aeration tank with no natural volatilization, Equation 24 is rewritten as

$$0 = Q (S_{in} - S) - Q_g H_c S - kSXV - (3.345 \times 10^{-7}) Q_w X K_{ow} S \quad (25)$$

All variables in the above equation are known, except for S, which can be determined by rearranging Equation 25:

$$S = \frac{Q}{Q + Q_g H_c + kXV + (3.345 \times 10^{-7}) Q_w X K_{ow}} S_{in} \quad (26)$$

Once S is known, the individual rates of removal can be calculated. A simplified sample calculation of the removal of ethylbenzene from an activated sludge tank with diffused aeration is provided in Appendix B.

## CHAPTER 3

### LITERATURE REVIEW OF VOC FATE MODELS

Several studies have been conducted in order to determine the overall fate of VOCs in wastewater treatment facilities. Some studies describe how samples taken at wastewater treatment facilities can be used to formulate emission factors or simple models to quantify VOC emissions; others present the mathematical models that have been developed to predict the fate of VOCs in wastewater treatment facilities. The paragraphs below describe some of the recent work that has been done to determine the fate of VOCs in wastewater treatment facilities.

Matter-Müller et al. (1981) discuss the relative importance of a number of parameters which affect VOC emissions from the wastewater to the atmosphere. These parameters include diffusivity, Henry's constant, the liquid and gas phase mass transfer coefficients, the air-water contacting pattern, and the presence of detergents (or surfactants). The authors discovered that volatilization rates are highly dependent upon the type of air-water contacting operation (such as surface or diffused aerated systems, stripping towers, etc.). Also, their results showed that the VOC emission rate from surface aerated systems and trickling filters is higher than the emission rate from diffused aerated systems.

Roberts and Dändliker (1983) studied the volatilization of six VOCs and oxygen from an aqueous solution to the atmosphere and described a methodology to quantify the emission rate from an agitated tank. They found that the overall mass transfer rate of the VOCs that they studied is proportional to the power input to the tank, and is approximately sixty percent of the oxygen mass transfer rate when the power input is kept constant. The proportionality is independent of the mixing intensity and is

calculated using the ratio of the diffusivities of the VOC and oxygen in water raised to a power approximately equal to 0.62.

Roberts et al. (1984) suggested models for estimating the volatilization of halogenated VOCs from an activated sludge system with either surface aeration or diffused aeration. The authors, however, did not consider the removal of VOCs by sorption to biological solids or by biodegradation. Their approach involved estimating the mass transfer rates of VOCs from that of oxygen, using proportionality coefficients determined in lab experiments. Although the models were not validated with field data, they predicted a lower volatilization rate during bubble aeration due to the greater saturation of the gas phase. Chrysikopoulos et al. (1992) used this model, along with a three dimensional atmospheric dispersion model, to predict VOC concentrations downwind of a wastewater treatment facility under neutral or stable atmospheric conditions.

Barton (1987) presented a model to examine the fate of influent organic chemicals in several biological treatment units, or more specifically, in an activated sludge system with surface or diffused aeration and an aerated stabilization basin. In addition to describing the distribution of organic compounds as a function of the physical properties of the compounds and the design and operating parameters of the system, this model considers the following removal mechanisms: forced air stripping via aeration, natural volatilization, biodegradation, and sorption to biological solids. The author tested this model with data from pulp and paper mill wastewater with low concentrations of four organic compounds (phenol, chloroform, tetrachloroguaiacol, and hexachlorobenzene). Natural volatilization was found to be insignificant for surface aerated systems due to the high efficiency of the aerators. However, in diffused aeration systems, natural volatilization was more significant. More data is needed to verify the model; however, the author suggests that it can be used as a "first-cut screening method" to estimate the

fate of certain organic compounds in biological treatment systems. This model has been computerized by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) and is called NOCEPM (NCASI Organic Compound Elimination Pathway Model).

Berglund and Whipple (1987) collected extensive samples of air, water, and sludge streams at a large wastewater treatment facility and, subsequently, used these data to assess the fate of eight VOCs in the treatment facility. The authors also developed simplistic models, based solely on Henry's constant, that predict the overall removal of these eight chemicals from selected treatment units.

Blackburn (1987) proposed a coupled removal mechanism equation which incorporated VOC sorption to biomass, stripping from reactor off-gas, biodegradation, and removal in the effluent. As in the other models, the author assumes steady-state conditions, a continuous feed to the reactor (an activated sludge unit with diffused aeration), and complete mixing within the reactor. In addition, first-order biodegradation and stripping rates are assumed.

Namkung and Rittmann (1987) developed a general fate model to estimate the removal of VOCs via volatilization, biodegradation, and sorption to biological solids in an activated sludge tank with diffused aeration, as well as determined the role of the individual removal mechanisms and their interactions. The model was tested using data from two Chicago wastewater treatment plants. Natural volatilization was neglected because the authors assumed that the main source for emissions to the air was the diffused aerated activated sludge tank. Sorption to biological solids was found to be negligible. The authors found that when the majority of VOCs present in the wastewater are biodegradable under aerobic conditions, biodegradation is the most important removal mechanism, and that when biodegradation occurs, volatilization and sorption are insignificant. However, if biodegradation is not significant, volatilization is

the primary removal mechanism. Namkung and Rittmann's model has been expanded and computerized into "EPA RATE (Fate and Treatability Estimator)" by ABB Environmental, Inc. for the Office of Water Regulations and Standards, Office of Water, EPA, Washington, DC.

BASTE (Bay Area Sewage Toxics Emissions) was developed for a group of publicly-owned treatment works (POTWs) in the San Francisco Bay Area by Corsi and Card (1991). BASTE is a computer-based model that predicts the removal of VOCs via volatilization (open atmosphere, diffused and surface aeration, volatilization at drop structures or weirs), biodegradation, and sorption to suspended solids and/or biomass. The model's most important feature is the "building block" approach used to simulate a variety of wastewater treatment processes. The building blocks include a series of continuous-flow stirred tank reactors with multiple options to describe aeration, quiescent surfaces, drop structures, packed media systems, and measured emissions or emission factors for those units which BASTE cannot simulate. These blocks can be placed in series or parallel and connected in order to form a flowsheet that simulates a wastewater treatment process. BASTE is also capable of modeling recycle streams and covered treatment units.

Govind et al. (1991), like Barton (1987), developed a mathematical model to estimate the distribution of influent organic chemicals based on the compounds' physical properties and on design and operating parameters of the wastewater treatment facility. However, the authors go a step further and model not only secondary treatment (a well-mixed aeration basin with a secondary clarifier), but also primary treatment (a primary clarifier). While the primary treatment system considers VOC removal via sorption and volatilization, the secondary system considers the following mechanisms: biodegradation, sorption, volatilization to the atmosphere, stripping via surface aeration, and stripping via diffused aeration. This model was validated using experimental data

from pilot-scale conventional activated sludge systems and provided good predictions for most compounds regulated by the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), with errors primarily due to errors in the biodegradation kinetic constants. It is generally known that literature values for biodegradation constants vary widely and are the primary source of errors in the estimation of VOC removal via biodegradation (Melcer, 1994). In order to alleviate this problem, the authors of this model used a group contribution method to estimate biodegradation kinetic constants. This model has been computerized and is called CINCI (EPA-Cincinnati Model).

Bell et al. (1993) conducted field investigations at two wastewater treatment facilities by collecting samples from the influent and effluent wastewater streams of aerated process vessels, namely, aerated grit removal chambers and diffused aeration activated sludge systems. Off-gas samples were also collected in order to formulate emission factors for the VOCs found in the off-gas stream. Unaccountable mass was assumed to be removed by biodegradation or some other mechanism. The study demonstrated that a wide range of VOCs are emitted from aerated process vessels, and that nonchlorinated compounds are more readily volatilized than chlorinated compounds. The authors also studied the effects of the aeration rate and biomass concentration on the emission rates and found that emissions to the atmosphere increase as the aeration rate increases and decrease as the biomass concentration increases.

Hsieh et al. (1993) used proportionality coefficients, as described by Matter-Müller et al. (1981) and Roberts et al. (1984), to estimate the overall mass transfer coefficient of a VOC from that of oxygen in a mechanically aerated tank. Since these methods tend to overestimate the removal of semivolatile compounds, the authors modified the proportionality coefficient to include the gas-phase mass transfer coefficient, which is important for estimating the mass transfer rates of compounds with

relatively low values of Henry's constant. They also formulated a relationship between the power input to the tank and the oxygen mass transfer coefficient, as well as between the power input and the ratio of the gas and liquid phase mass transfer coefficients of the VOC. In another study, Hsieh et al. (1993) applied the modified proportionality coefficient concept to diffused aerated tanks and correlated the ratio of the gas and liquid phase mass transfer coefficient to the specific air flowrate into the tank.

Parker et al. (1993), in addition to studying the importance of volatilization, biodegradation, and sorption in activated sludge aeration basins, examined the significance of diffuser type and air flowrate on the rate of volatilization. The authors were also able to successfully simulate emissions from a full-scale aeration basin in a pilot plant.

The EPA (1994) has published a technical report (EPA-453/R-94-080A) entitled "Air Emissions Models for Waste and Wastewater," which contains important equations used in estimating VOC emissions not only from wastewater treatment tanks and collection systems but also from disposal impoundments (including nonaerated disposal impoundments), land treatment, and landfills. The EPA has also developed three computer models to predict the fate of VOCs in wastewater treatment facilities. WATER8 contains analytical models for estimating compound-specific air emissions for wastewater treatment facilities and collection systems. CHEMDAT8 also estimates VOC emissions from treatment, storage, and disposal facility processes, and SIMS (Surface Impoundment Modeling System) predicts air emissions from surface impoundments and wastewater collection devices.

Mayer et al. (1994) presented the results of air toxics emissions inventory reports from four POTWs in Los Angeles, California. The authors used this data to compare the estimation methods currently available and prepare health risk assessments to



determine the potential impact of the facilities' emissions on their employees and on neighboring residents.

Melcer et al. (1994) developed another computer-based fate model, called TOXCHEM (Toxic Chemical Modeling Program for Water Pollution Control Plants), to estimate the removal of VOCs by volatilization, biodegradation, and sorption in grit chambers, aeration basins, and primary and secondary clarifiers. The model was calibrated in pilot-plant experiments to determine biodegradation rate constants, solid/liquid partition coefficients, and Henry's constants. Data from municipal and industrial wastewater treatment plants was used to verify the model. The unique feature of TOXCHEM is that, in addition to simulating steady-state conditions, it is capable of modeling dynamic conditions in a treatment process.

Peng et al. (1994) studied the emissions of benzene, toluene, trichloroethylene, and tetrachloroethylene from a tank with a quiescent water surface and with no flow in or out of the tank. They developed mathematical models, using Fick's Law, to describe the volatilization rate of the VOCs from the tank. The model was derived by solving a partial differential equation, which was simplified for practical use. The volatilization rate constant was found to be inversely proportional to the square of the water depth in the tank, whereas in a completely mixed tank, the volatilization rate is inversely proportional to the water depth. In a more recent study, the authors developed, calibrated, and verified a model for the volatilization of VOCs from agitated tanks (Peng et al., 1995). The volatilization rate was correlated with the surface area to volume ratio of the tank and the turbulent intensity.

In general, the models mentioned above use similar equations to estimate the removal of VOCs and differ only in the mass transfer assumptions and the methods used to calculate rate coefficients (i.e., oxygen transfer coefficients, biodegradation constants, etc.). Differences in VOC removal estimates from different models can be

attributed to these factors, as well as variations in the physical and chemical properties of the chemical under consideration (Card and Desing, 1994). In addition, some models estimate VOC removal from activated sludge systems only, while others determine removal rates from a wider variety of treatment units. None of the models, however, completely predicts the removal of VOCs from an entire wastewater treatment facility, including sludge treatment. Two review articles (Mihelcic et al., 1993; Melcer, 1994) provide the equations commonly used to predict volatilization rates from wastewater treatment facilities. In addition, Melcer (1994) presents the models for biodegradation and sorption, as well as a review of the computer-based fate models that are currently available.

## CHAPTER 4

### IMPLEMENTATION OF VOLATILIZATION MODELS IN ENVIROCAD

#### 4.1 EnviroCAD

EnviroCAD is a process simulator used for analyzing and refining integrated wastewater treatment processes. The main features of EnviroCAD include performing component-specific material balances, estimating environmental stream properties, and providing an economic analysis of the treatment system under study. EnviroCAD can also be used to examine the effects of changes in operating conditions on the performance of the entire system, as well as evaluate possible waste minimization alternatives. The incorporation of VOC volatilization, or emission, models to the process simulator will add a new dimension to its capabilities.

#### 4.2 Volatilization Models in EnviroCAD

The important equations used to estimate the removal of VOCs via volatilization, biodegradation, and sorption were provided in Chapter 2. The equations presented in the next four sections are for volatilization only and have been implemented in EnviroCAD as a part of this thesis. These equations are straightforward and depend upon design and operating parameters, which are common inputs to EnviroCAD. Models for biodegradation already exist in EnviroCAD. Currently, sorption to solids is not considered since it is not a significant VOC removal mechanism.

##### 4.2.1 Volatilization Models for Quiescent Surfaces

The removal of VOCs from tanks with quiescent surfaces (equalizers, neutralizers, clarifiers, thickeners, etc.) occur due to natural volatilization, i.e., mass transfer across

open surfaces. In order to calculate these emissions, the overall mass transfer coefficient,  $K_L$ , of the VOC must be calculated, where

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{H_c k_g} \quad (27)$$

and  $k_l$ ,  $k_g$ , and  $H_c$  have been defined previously. Values of  $H_c$  and other physical properties of VOCs, such as viscosities, densities, and diffusivities, are read from a database linked to EnviroCAD.

Two separate models have been implemented into EnviroCAD in order to calculate the individual mass transfer coefficients of VOCs from quiescent surface tanks. The user can choose which model to use to calculate the liquid and gas phase mass transfer coefficients.

The first model estimates  $k_l$  and  $k_g$  using the correlations developed by Mackay and Yeun (1983), where

$$k_l = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} U^* Sc_L^{-0.5} \quad \text{for } U^* > 0.3 \quad (28)$$

$$k_l = 1.0 \times 10^{-6} + 144 \times 10^{-4} U^{*2.2} Sc_L^{-0.5} \quad \text{for } U^* < 0.3 \quad (29)$$

$$k_g = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} U^* Sc_G^{-0.67} \quad (30)$$

and,

$$U^* = (6.1 + 0.63U_{10})^{0.5} U_{10} \quad (31)$$

where  $U_{10}$  is the wind velocity at ten meters above the surface of the liquid in (m/s) and is a user input to EnviroCAD.  $Sc_L$  and  $Sc_G$  are the Schmidt numbers of the VOC in the liquid and gas phases, respectively, and are given by the following equations:

$$Sc_L = \frac{\mu_L}{\rho_L D_w} \quad (32)$$

and

$$Sc_G = \frac{\mu_G}{\rho_G D_a} \quad (33)$$

where  $\mu_L$  and  $\mu_G$  are the viscosities of water and air in (g/cm s), respectively.  $\rho_L$  and  $\rho_G$  are the densities of air and water in (g/cm<sup>3</sup>), respectively, and  $D_w$  and  $D_a$  are the diffusivities of the VOC in water and in air in (cm<sup>2</sup>/s), respectively.

The second model, which is used by the EPA, utilizes three correlations formulated by Springer et al. (1984) to estimate the liquid phase mass transfer coefficient for the VOC. These correlations are based upon the wind speed at ten meters ( $U_{10}$ ) above the liquid surface and the fetch-to-depth ratio ( $F/D$ ) of the tank under consideration. "Fetch" is the linear distance across the tank (EPA, 1994).

For all  $F/D$  ratios and  $0 < U_{10} < 3.25$  m/s,

$$k_l = 2.78 \times 10^{-6} \left( \frac{D_w}{D_{ether}} \right)^{0.67} \quad (34)$$

For  $14 < F/D < 51.2$  and  $U_{10} > 3.25$  m/s,

$$k_l = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] U_{10}^2 \left( \frac{D_w}{D_{ether}} \right)^{0.67} \quad (35)$$

And, for  $F/D > 51.2$  and  $U_{10} > 3.25$  m/s,

$$k_l = 2.611 \times 10^{-7} U_{10}^2 \left( \frac{D_w}{D_{ether}} \right)^{0.67} \quad (36)$$

where  $D_w$  and  $D_{ether}$  are the diffusivities of the VOC and ether in water, respectively, in  $(\text{cm}^2/\text{s})$ . For cases where  $F/D < 14$  and  $U_{10} > 3.25$  m/s, the correlations developed by Mackay and Yeun (1983) for the liquid phase mass transfer coefficient are used.

In order to calculate the gas phase mass transfer coefficient, the EPA uses the equation developed by Mackay and Matasugu (Hwang, 1982):

$$k_g = 4.82 \times 10^{-3} U^{0.78} Sc_G^{-0.67} d_e^{-0.11} \quad (37)$$

where  $U$  is the wind speed in (m/s) and  $d_e$  is the effective diameter of the tank in (m), or

$$d_e = \left( \frac{4A}{\pi} \right)^{0.5} \quad (38)$$

$A$  is the surface area of the tank in  $(\text{m}^2)$ , which is either calculated by EnviroCAD or specified by the user.

Once  $k_l$  and  $k_g$  have been estimated, the overall mass transfer coefficient can be calculated using Equation 27, and the overall rate of VOC emissions across an open surface can be determined from the following equation, assuming that the accumulation of VOCs in the gas phase is negligible:

$$R_{vol} = - K_L A C_l \quad (39)$$

where  $C_l$  has been defined previously.

#### 4.2.2 Volatilization Models for Aerated Tanks

The fundamental equations necessary to estimate volatilization from aerated tanks (mechanical surface and diffused aerated tanks) were described in Sections 2.1.2 and 2.1.3. In order to calculate the emissions from the aeration basin, the overall mass transfer coefficient of the VOC must be calculated. The mass transfer rates of the individual VOCs are estimated from that of oxygen, using a proportionality coefficient,  $\psi_M$  (Hsieh et al., 1993):

$$(K_L a)_{\text{VOC}} = \psi_M (K_L a)_{\text{O}_2} \quad (40)$$

where  $(K_L a)_{\text{VOC}}$  and  $(K_L a)_{\text{O}_2}$  are the overall transfer rate constants for a VOC and dissolved oxygen in ( $\text{s}^{-1}$ ), respectively. The value of  $(K_L a)_{\text{O}_2}$  in the wastewater is a user input in EnviroCAD; however,  $\psi_M$  is given by the following equation (Hsieh et al., 1993):

$$\psi_M = \psi \left( 1 + \frac{1}{H_c \frac{k_{ga}}{k_{la}}} \right)^{-1} \quad (41)$$

$\psi$  has been defined previously in Chapter 2 and can be assumed to be approximately 0.6 or calculated using the diffusivities of the VOC and oxygen in water (see Equation 8).  $k_{ga}$  and  $k_{la}$  are the individual mass transfer coefficients of the VOC in the gas and liquid phases, respectively, in ( $\text{s}^{-1}$ ). For mechanically aerated systems, the value of  $k_{ga}/k_{la}$  is estimated using the following equation (Hsieh et al., 1993):

$$\log \left( \frac{k_{ga}}{k_{la}} \right) = -1.85 \log (P/V) + 2.43 \quad (42)$$

P and V have been defined previously, and (P/V) is calculated by EnviroCAD. For diffused aerated systems, the value of  $k_g a/k_l a$  will be set by the user or it will be assumed that the compound is highly volatile and that  $\psi_M = \psi$ . Once  $\psi$  or  $\psi_M$  is known, the overall mass transfer coefficient,  $(K_L a)_{VOC}$ , is calculated by Equation 40.

Once  $(K_L a)_{VOC}$  has been determined, the rate of volatilization from mechanically aerated systems or from diffused aerated systems is estimated. Emissions due to mechanical surface aeration in an aeration basin are calculated with the following equation:

$$R_{vol} = - (K_L a)_{VOC} C_l V \quad (43)$$

where  $C_l$  and V have been defined previously. The rate of a VOC's volatilization from a diffused aeration tank is given as follows:

$$R_{vol} = - Q_g H_c C_l \left\{ 1 - \exp \left( - \frac{(K_L a)_{VOC} V}{H_c Q_g} \right) \right\} \quad (44)$$

or,

$$R_{vol} = - Q_g H_c C_l \left\{ 1 - \exp \left( - \frac{\psi_M (K_L a)_{O_2} V}{H_c Q_g} \right) \right\} \quad (45)$$

#### 4.2.3 Volatilization Model for Trickling Filters

To estimate emissions from trickling filters, EnviroCAD utilizes the same method Corsi and Card (1991) use in their BASTE model. Basically, the trickling filter is modeled as a packed-media system in which volatilization is the primary removal mechanism for all VOCs (Corsi and Card, 1991), a conservative assumption for VOCs that are aerobically degradable. According to Metcalf and Eddy (1991), aerobically degradable VOCs must



first adsorb onto the biological slime layer of the trickling filter prior to being biodegraded. As mentioned in Chapter 2, sorption of VOCs onto biomass (in this case, the biological slime layer) is negligible when compared to volatilization.

The mass balance for a particular VOC around a trickling filter operating countercurrently is written as follows:

$$Q (C_{l,in} - C_{l,out}) = Q_g (C_{g,out} - C_{g,in}) \quad (46)$$

where  $Q$  is the wastewater flowrate in ( $\text{m}^3/\text{s}$ ) and  $Q_g$  is either the natural or forced air ventilation rate, or aeration rate, in ( $\text{m}^3/\text{s}$ ).  $C_{l,in}$  and  $C_{l,out}$  are the influent and effluent concentrations of the VOC in the wastewater in ( $\text{g}/\text{m}^3$ ), respectively.  $C_{g,in}$  and  $C_{g,out}$  are the initial and final concentrations of the VOC in the air in ( $\text{g}/\text{m}^3$ ), respectively. Since the initial concentration of the VOC in the circulating air,  $C_{g,in}$ , is zero prior to the wastewater entering the trickling filter, Equation 46 becomes:

$$Q (C_{l,in} - C_{l,out}) = Q_g (C_{g,out}) \quad (47)$$

Corsi and Card (1991) also make the assumption that the VOCs in the effluent air stream are in thermodynamic equilibrium with VOCs in the influent wastewater stream, or that

$$C_{g,out} = H_c C_{l,in} \quad (48)$$

where  $H_c$  is the dimensionless Henry's constant. Equation 47 is then rewritten as

$$Q (C_{l,in} - C_{l,out}) = Q_g H_c C_{l,in} \quad (49)$$

Equation 49 can then be solved for  $C_{l,out}$ . However, since  $Q (C_{l,in} - C_{l,out})$  is equal to the emissions rate, only the terms on the right hand side of Equation 49 need to be known in order to determine the rate of volatilization of a VOC from a countercurrent trickling filter.

To determine the rate of a VOCs emission from a cocurrent trickling filter, the same assumptions and the same mass balance are made. However, the equilibrium relation is written differently. In this case, since the trickling filter is operating cocurrently, the effluent air and wastewater streams are assumed to be in thermodynamic equilibrium, or

$$C_{g,out} = H_C C_{l,out} \quad (50)$$

The overall mass balance then becomes

$$Q (C_{l,in} - C_{l,out}) = Q_g H_C C_{l,out} \quad (51)$$

Equation 51 is then solved for  $C_{l,out}$ . Once  $C_{l,out}$  is known, the volatilization rate of a VOC,  $Q(C_{l,in} - C_{l,out})$  or  $Q_g H_C C_{l,out}$ , can be determined.

#### 4.2.4 Volatilization Model for Junction Boxes

One or more wastewater streams can flow into a junction box prior to entering the next treatment unit of a wastewater treatment process. If these junction boxes are open to the atmosphere, VOC emissions occur in the same manner as emissions from quiescent surface tanks occur, except the liquid phase mass transfer coefficient is given by the following empirical equation (EPA, 1994):

$$k_l = 1.41 \times 10^{-4} \left( \frac{v^{0.67}}{d^{0.85}} \right) \left( \frac{D_w}{0.000021} \right)^{0.83} \quad (52)$$

where  $v$  is the waste velocity in (cm/s) and is calculated by dividing the wastewater flowrate by both the depth of the liquid inlet flow into the junction box,  $d$ , and width of the junction box (or, the square root of the area of the liquid surface).  $D_w$  is the diffusivity of the VOC in water in (cm<sup>2</sup>/s) and 0.000021 is the diffusivity of the reference liquid in (cm<sup>2</sup>/s).

The depth,  $d$ , can be estimated two different ways depending on the location of the inlet pipe. If the pipe is submerged below the surface of the wastewater, the depth is equal to the pipe's internal diameter plus the distance the pipe is submerged under the surface of the liquid in the junction box. If the location of the wastewater discharge is at the surface of the liquid in the junction box, then the depth of flow is considered to be half of the pipe's internal diameter.

The gas phase mass transfer coefficient is calculated by the correlation developed by Mackay and Yeun (1983). The overall mass transfer coefficient and the rate of volatilization can then be calculated by Equations 27 and 39, respectively.

## CHAPTER 5

### EXAMPLE AND SENSITIVITY ANALYSIS

#### 5.1 Illustrative Example

The use of EnviroCAD for the prediction of the fate of VOCs in wastewater treatment facilities is demonstrated in the following example. A typical wastewater treatment facility, as represented by EnviroCAD, is shown in Figure 1. The pretreatment section utilizes an equalization basin (EQ-101) to eliminate temporal fluctuations in the flowrate and composition of the influent wastewater stream (S-101). A primary clarifier (CL-101) is used to remove any suspended solids in the wastewater. Secondary treatment units include a mechanical surface aeration basin (AEB-101) to accomplish the biological oxidation of the organic materials present in its feedstream (S-107) and a secondary clarifier (CL-102) to remove the sludge and any solids not removed by previous treatment. A fraction of the sludge (S-113) is recycled back to the aeration basin in order to maintain a constant biomass concentration in the tank. The excess sludge from the secondary clarifier (S-114), as well as the sludge from the primary clarifier (S-106), are sent for sludge treatment, which will not be discussed in this example.

This particular wastewater treatment facility treats approximately 4.6 million gallons of wastewater per day. The composition of the influent wastewater stream is shown in Table 5. All of the chemicals listed are considered hazardous and are regulated by the EPA. Other contaminants, such as suspended solids, inorganic compounds, and heavy metals, may be present in the wastewater, but will not be considered in this example.

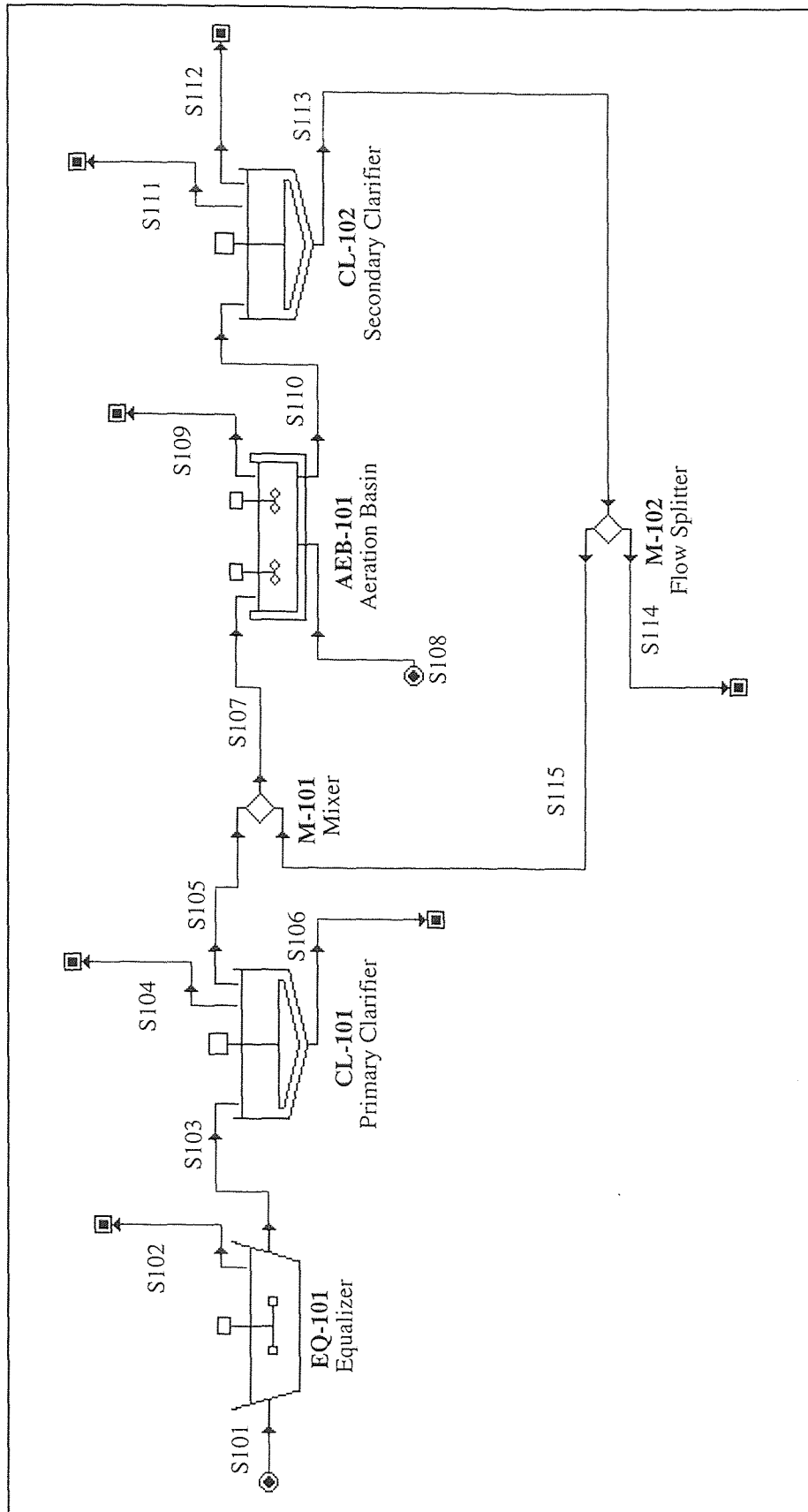


Figure 1 Example Wastewater Treatment Facility

**Table 5** Composition of Influent Wastewater Stream (kg/h).

Compound	Flowrate (kg/h)
Water	787,000
Benzene	40
Dichloroethane	20
Ethylbenzene	45
Phenol	50
Tetrachloroethylene	25
Toluene	25
1,1,1-trichloroethane	35

The chemical, physical, and environmental properties of each chemical under consideration are contained in a database linked to EnviroCAD. Once the flowrates of the chemicals, as well as the operating conditions of each unit, are specified, EnviroCAD carries out the component-specific mass balances, which are important for studying the fate of VOCs. The overall mass balance generated by EnviroCAD for this example is provided in Appendix C.

The temperature throughout the example treatment facility is kept constant at 25 °C and the windspeed is assumed to be 3.5 m/s. The equations formulated by Springer et al. (1984) were used to calculate the VOC emissions from each quiescent surface tank. The fate of each compound present in the influent wastewater stream is provided in Table 6, and the VOC volatilization rates from each unit in the example are summarized in Table 7. The results shown in Table 7 indicate that this facility emits more than 25 tons of VOCs per year. It is, therefore, considered a major source of VOC emissions according to the Clean Air Act Amendments of 1990, and appropriate measures should be undertaken to reduce VOC emissions from this facility.

It is also important to perform sensitivity analyses to determine how VOC emissions rates are influenced by changes in process operating conditions. The effects of some of these changes on the example facility are examined in the next section.

**Table 6** Fate of VOCs in the Example Treatment Facility.

Chemical	Influent Flowrate (kg/h)	Effluent Flowrate (kg/h)	Percent Removal by Volatilization (%)	Percent Removal by Biodegradation (%)
Benzene	40	2.2564	20.4	73.9
Dichloroethane	20	1.9193	33.3	57.1
Ethylbenzene	45	5.9702	40.5	46.3
Phenol	50	1.0475	0.2	97.7
Tetrachloroethylene	25	2.9096	38.7	49.7
Toluene	25	0.6040	9.3	88.3
1,1,1-trichloroethane	35	5.3851	52.2	32.5
Total VOCs	240	20.0921	26.4	65.2

**Table 7** VOC Emissions from the Treatment Units in the Example (kg/h).

Chemical	EQ-101	CL-101	AEB-101	CL-102
Benzene	0.0699	0.7741	7.3089	0.0163
Dichloroethane	0.0392	0.4331	6.1729	0.0156
Ethylbenzene	0.0676	0.7508	17.3563	0.0372
Phenol	0.0089	0.0854	0.0076	0.0007
Tetrachloroethylene	0.0389	0.4314	9.1856	0.0187
Toluene	0.0401	0.4445	1.8326	0.0040
1,1,1-trichloroethane	0.0570	0.6324	17.5300	0.0364
Total VOCs	0.3216	3.5517	59.3938	0.1289

## 5.2 Sensitivity Analysis

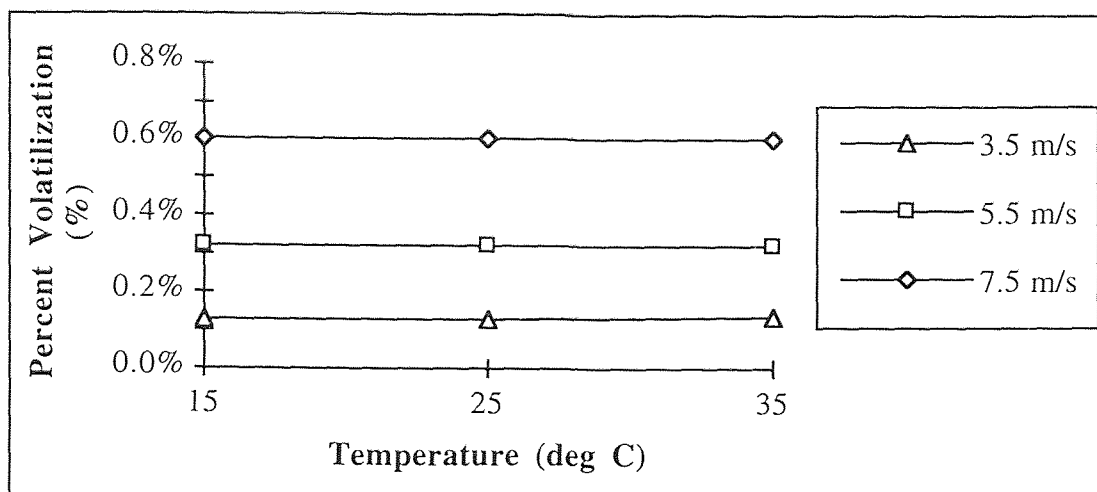
As mentioned in Chapter 4, EnviroCAD includes mathematical models for a variety of wastewater treatment unit operations that can be connected to simulate an entire wastewater treatment system. This capability allows users of EnviroCAD to easily examine the effects of changes in design and operating conditions on the system's performance. In the following paragraphs, the effects of variations in windspeed, temperature, and clarifier detention time on the VOC volatilization rates from the example described in Section 5.1 are studied.

The effect of changes in the windspeed are examined first. The results show that a step change in windspeed from 3.5 m/s to 5.5 m/s increases the overall emission rate (shown as percent volatilization) from each quiescent surface tank, as expected, by a factor of approximately 2.3 to 2.5. Similarly, another step change from 5.5 m/s to 7.5 m/s also resulted in an increase in the emissions rate by a factor of 1.8 to 2. This behavior can be explained by studying the correlations used to estimate the VOC emissions. In these cases, the correlations formulated by Springer et al. (1984) are used to calculate the emissions rates (see Section 4.2.1). Generally, an increase in the windspeed results in an increase in the overall mass transfer coefficient and, subsequently, the overall emissions rate. This type of behavior can also be observed when the correlations developed by Mackay and Yeun (1983) are used to calculate the rate of VOC removal by volatilization.

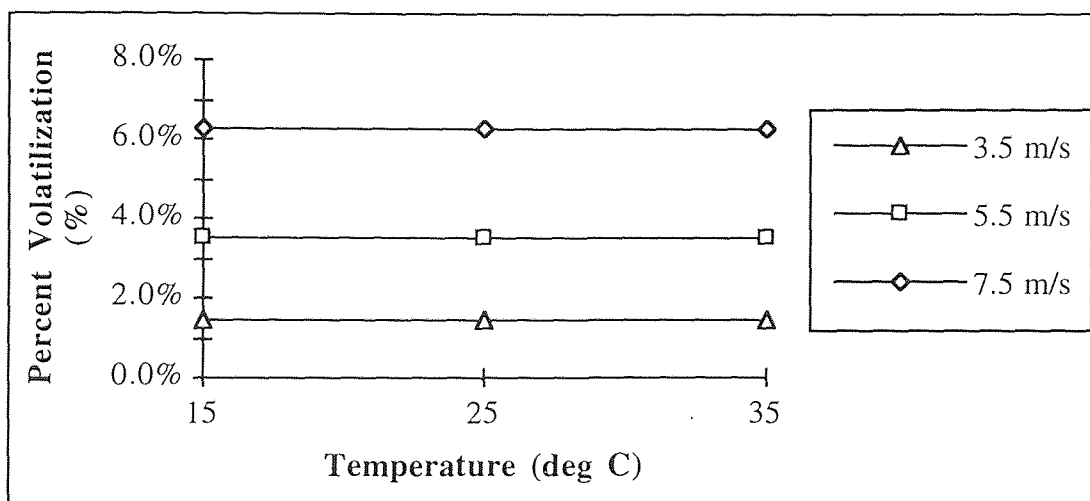
Changes in the rates of volatilization (shown as percentages removed from the tank) from the equalization basin, primary clarifier, and secondary clarifier with changes in the windspeed at three different temperatures (15 °C, 25 °C, and 35 °C) are shown in Figures 2, 3, and 4, respectively. The results show that windspeed has an effect on the volatilization rates from the quiescent surface tanks (EQ-101, CL-101, and CL-102), and has no effect on the emissions from the aeration basin (AEB-101).

Changes in temperature had no effect on the volatilization rates of the volatile compounds (benzene, dichloroethane, ethylbenzene, tetrachloroethylene, toluene, and 1,1,1-trichloroethane). The emission rate of the relatively nonvolatile compound (phenol), however, was effected. The value of the dimensionless Henry's constant,  $H_C$ , was used to distinguish the volatile compounds from the nonvolatile compound. Phenol had a relatively low Henry's constant compared to the other six compounds and, therefore, was considered nonvolatile.

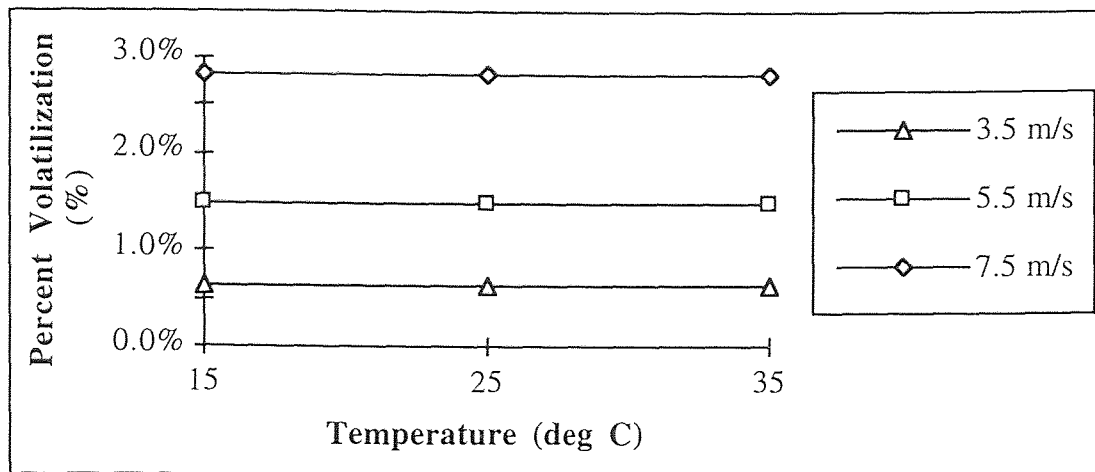




**Figure 2** Effect of Windspeed and Temperature on Volatilization Rates in the Equalization Basin



**Figure 3** Effect of Windspeed and Temperature on Volatilization Rates in the Primary Clarifier



**Figure 4** Effect of Windspeed and Temperature on Volatilization Rates in the Secondary Clarifier

The temperature effects can be seen in the following equation:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{H_c k_g} \quad (53)$$

For volatile compounds, the gas phase resistance is not important and the overall mass transfer coefficient depends on the value of  $k_l$  and is therefore independent of temperature. For nonvolatile compounds, since the second term on the right-hand side of Equation 53 can no longer be neglected, the temperature dependence of  $H_c$  becomes important.

To study the effects of detention time, the detention time of the primary clarifier was changed from 7.2 hours to 72 hours. The rates of VOC volatilization in the primary clarifier for each of these cases are shown in Table 8. In general, longer detention times in quiescent tanks result in an increase in the overall volatilization rates of each VOC. Similarly, emissions from tanks with shorter detention times are reduced.

**Table 8** Effect of Detention Time on Volatilization Rates in the Primary Clarifier.

Chemical	Percent Volatilization (%) (Detention time = 7.2 h)	Percent Volatilization (%) (Detention time = 72 h)
Benzene	1.94	16.91
Dichloroethane	2.17	18.59
Ethylbenzene	1.67	14.89
Phenol	0.17	1.69
Tetrachloroethylene	1.73	15.33
Toluene	1.78	15.73
1,1,1-trichloroethane	1.81	15.95

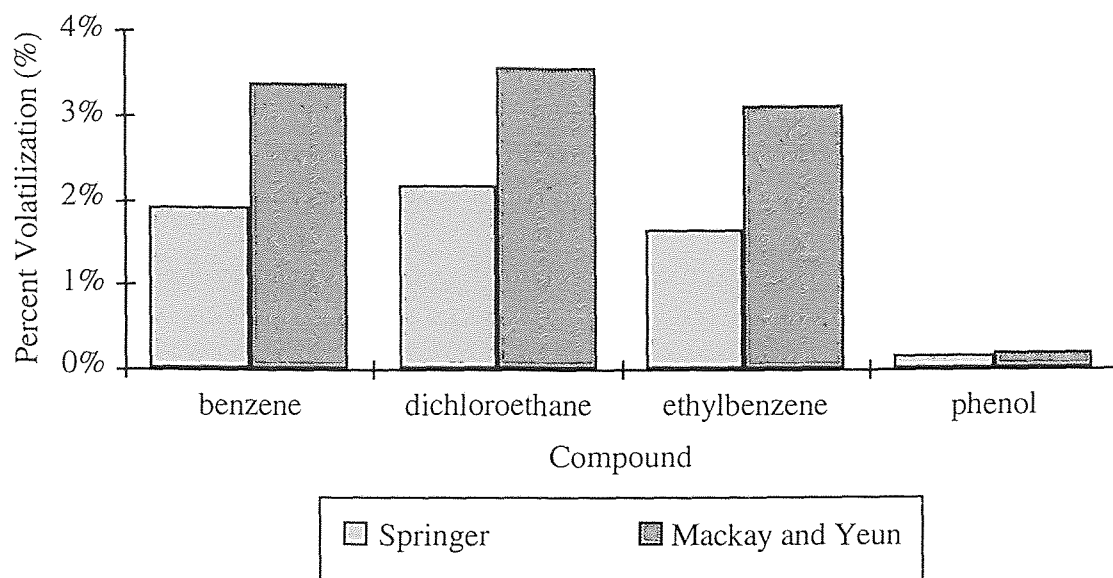
In addition to studying the effects of windspeed, temperature, and clarifier detention time, the consequences of using a diffused aeration basin and the correlations of Mackay and Yeun (1983) on the emissions rates of VOCs were also investigated.

A comparison of the volatilization rates from a mechanical surface aeration basin and a diffused aeration basin is shown in Table 9 below. The results support Roberts' et al. (1984) theory that lower volatilization rates are predicted during diffused aeration because of the greater saturation of the gas phase.

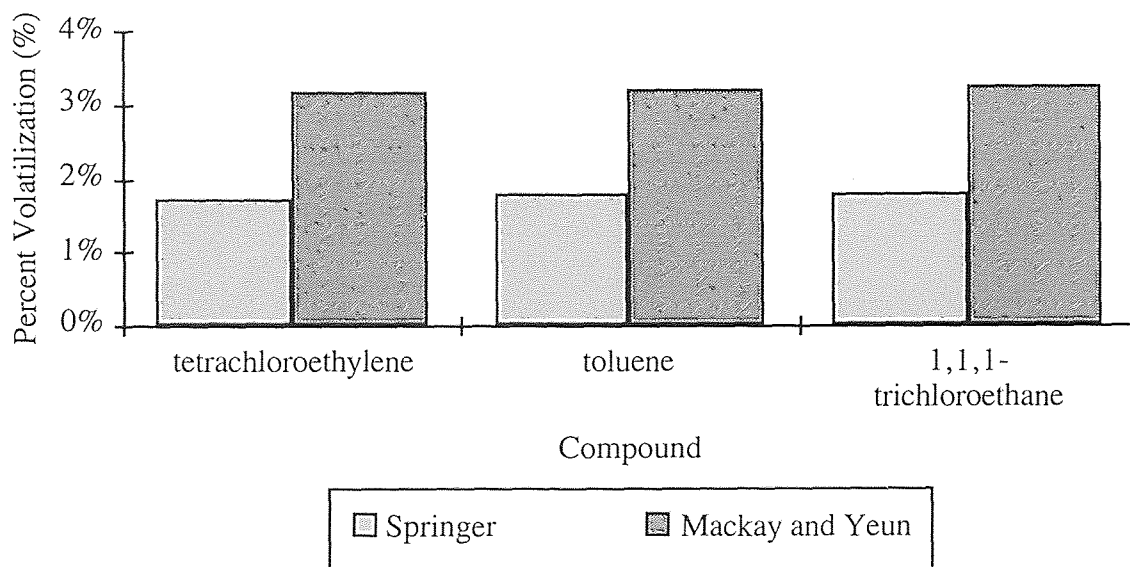
**Table 9** Comparison of VOC Emission Rates in Aerated Tanks.

Chemical	Percent Volatilization (%) from a Mechanical Surface Aeration Basin	Percent Volatilization (%) from a Diffused Aeration Basin
Benzene	18.7	17.0
Dichloroethane	31.6	26.0
Ethylbenzene	39.2	36.7
Phenol	0.02	0.002
Tetrachloroethylene	37.4	36.6
Toluene	7.5	7.0
1,1,1-trichloroethane	51.1	49.5

The use of Mackay and Yeun's correlations to predict emissions rates from quiescent surface tanks result in higher volatilization rates for each compound. The comparison of the emissions from the primary clarifier is shown in Figures 5 and 6.



**Figure 5** Comparison of Emissions Correlations for benzene, dichloroethane, ethylbenzene, and phenol in the Primary Clarifier



**Figure 6** Comparison of Emissions Correlations for tetrachloroethylene, toluene, and 1,1,1-trichloroethane in the Primary Clarifier

## CHAPTER 6

### CONCLUSIONS

The 1990 Clean Air Act Amendments have designated wastewater treatment facilities as major sources of VOC emissions. As a result of increasingly strict environmental regulations, these facilities are now being pressured to assess the fate of VOCs during each step of their treatment processes and, ultimately, control the release of VOCs from their facilities. Subsequently, the demand for models which can accurately predict the fate of VOCs in integrated wastewater treatment processes has increased. Although many models have been developed to perform this task, no model completely predicts emissions from an entire wastewater treatment facility. This thesis presents models for estimating the removal of VOCs through volatilization from several treatment units often found in wastewater treatment facilities. These models have been implemented into EnviroCAD, an environmental process simulator. One application of these models is demonstrated in an illustrative example.

A sensitivity analysis on the example wastewater treatment facility presented in this thesis showed that volatilization rates increase with increasing windspeed. The emissions of volatile compounds are not dependent upon temperature, while the emissions of relatively nonvolatile compounds are effected because the gas phase resistance and the temperature dependence of Henry's constant become important. Using diffused aeration instead of mechanical surface aeration results in lower volatilization rates from the aeration basin. Also, VOC emissions rates are sensitive to the correlations used to predict the emissions.

The example and sensitivity analysis presented also show the feasibility of using models to predict the fate of VOCs in wastewater treatment facilities. With the

automation of these models into simulators, such as EnviroCAD, quick and easy assessments of the total environmental impact of an existing or conceptual wastewater treatment facility can be made. Simulators can also facilitate the design of VOC control technologies, as well as the analysis of a number of possible waste minimization schemes.

## APPENDIX A

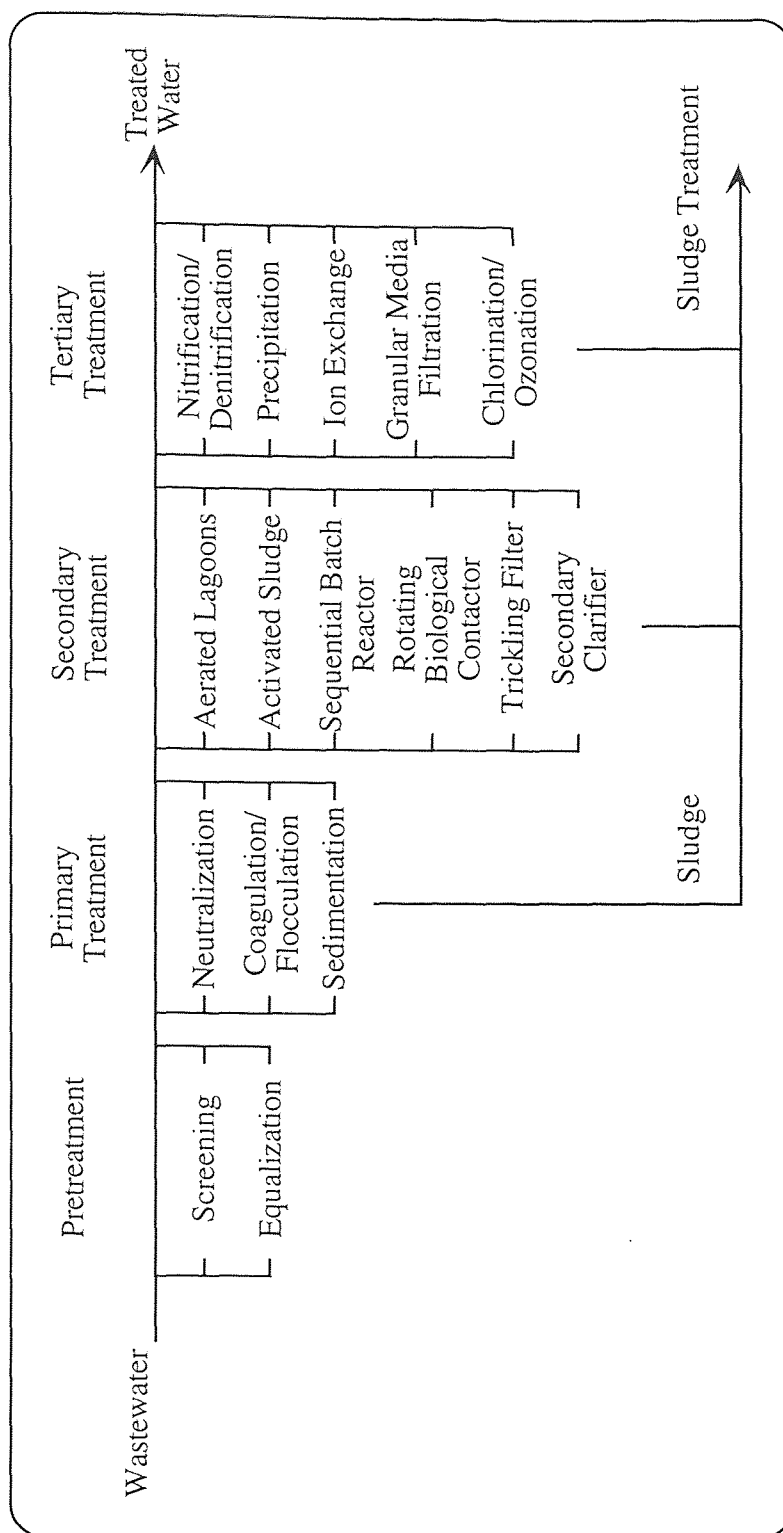
### DESCRIPTION OF A WASTEWATER TREATMENT FACILITY

Typical wastewater treatment facilities are designed to remove the following categories of pollutants from industrial or municipal wastewater streams:

- soluble organics
- heavy metals
- acidity and alkalinity
- oils, grease, and other floating materials
- nutrients (nitrogen and phosphorus)
- suspended and colloidal solids
- color, turbidity, and odors
- priority pollutants

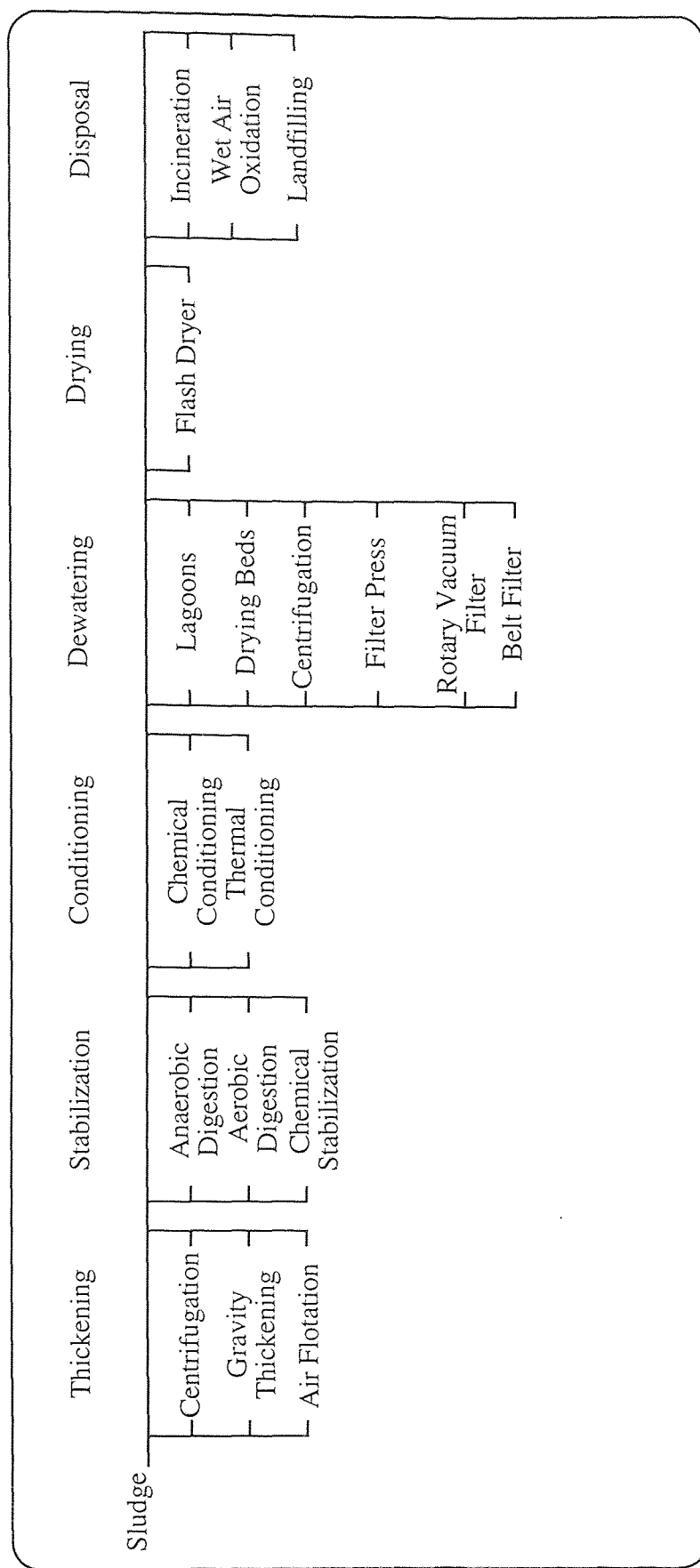
To remove or reduce these contaminants from a wastewater stream, wastewater treatment facilities employ various treatment processes, often termed pretreatment, primary treatment, secondary treatment, tertiary treatment, and sludge treatment processes. Usually, some combination of one or more of these processes is used to clean the wastewater stream. The extent of treatment depends upon the source and prior use of the wastewater stream. The typical unit operations used in wastewater and sludge treatment are shown in Figures A1 and A2.

Pretreatment utilizes screening to remove large solid particles and equalization to eliminate temporal fluctuations in the flowrate and composition of the influent wastewater stream. During primary treatment, neutralization is used to reduce the



**Figure A1** Typical Unit Operations for Wastewater Treatment





**Figure A2** Typical Unit Operations for Sludge Treatment

acidity or alkalinity of wastewater streams. In addition, oils, grease, and suspended solids are removed from the wastewater stream by flotation, sedimentation or clarification, or filtration. Secondary treatment utilizes biological organisms to degrade soluble organic compounds. Tertiary treatment, or advanced wastewater treatment, occurs after secondary treatment to remove specific types of waste, such as colloidal solids by filtration and organics by adsorption or chemical oxidation (Eckenfelder et al., 1985). Processes such as precipitation, activated carbon adsorption, chemical oxidation, stripping, ion exchange, reverse osmosis, and electrodialysis are used to remove or reduce materials like heavy metals, pesticides, and nutrients that remain untreated after passing through prior treatment steps (Eckenfelder et al., 1985). During sludge treatment, sludge is typically thickened and dewatered prior to disposal or destruction. Sludge can also be anaerobically digested, thermally treated, or oxidized in order to reduce its mass or to make its disposal easier (Eckenfelder et al., 1985).

## APPENDIX B

### SAMPLE CALCULATION OF THE REMOVAL OF ETHYLBENZENE FROM AN ACTIVATED SLUDGE TANK

A mass balance for ethylbenzene in a well-mixed activated sludge tank is written as follows (see Equation 23):

$$V \frac{dS}{dt} = QS_{in} - Q_e S - Q_w S + R_{vol} + R_{bio} + R_{sor} \quad (B1)$$

where	$V \text{ (m}^3\text{)}$	= volume of the tank
	$S \text{ (g/m}^3\text{)}$	= concentration of the compound in the tank
	$t \text{ (s)}$	= time
	$Q \text{ (m}^3\text{/s)}$	= wastewater flowrate into the tank
	$S_{in} \text{ (g/m}^3\text{)}$	= concentration of the compound in the influent stream
	$Q_e \text{ (m}^3\text{/s)}$	= effluent flowrate
	$Q_w \text{ (m}^3\text{/s)}$	= sludge flowrate
	$R_{vol} \text{ (g/s)}$	= rate of compound removal by volatilization
	$R_{bio} \text{ (g/s)}$	= rate of compound removal by biodegradation
	$R_{sor} \text{ (g/s)}$	= rate of compound removal by sorption

Assuming steady-state conditions and that the sum of the effluent flowrate and the sludge flowrate equals the influent wastewater flowrate, Equation B1 is reduced to

$$0 = Q(S_{in} - S) + R_{vol} + R_{bio} + R_{sor} \quad (B2)$$

For example, for a diffused aeration tank, Equation B2 is rewritten as

$$0 = Q (S_{in} - S) - Q_g H_c S - kSXV - (3.345 \times 10^{-7}) Q_w X K_{ow} S \quad (B3)$$

or,

$$S = \frac{Q}{Q + Q_g H_c + kXV + (3.345 \times 10^{-7}) Q_w X K_{ow}} S_{in} \quad (B4)$$

The rate of volatilization for the tank assumes that the air bubbles become fully saturated with a VOC during transport through wastewater (See Section 2.1.3 on stripping by diffused aeration) and that natural volatilization is negligible.

Table B1 provides the assumptions made in order to calculate the removal rate of ethylbenzene in an activated sludge tank with diffused aeration.

**Table B1** Assumptions for Estimation of the Removal of Ethylbenzene from an Activated Sludge Tank with Diffused Aeration.

Parameter	Value of Parameter
V	200,000 m <sup>3</sup>
Q	870,000 m <sup>3</sup> /d
S <sub>in</sub>	0.018 g/m <sup>3</sup> (18 µg/L)
Q <sub>g</sub>	5,000,000 m <sup>3</sup> /d
X <sub>a</sub>	2000 g VSS/m <sup>3</sup>
Q <sub>w</sub>	13,000 m <sup>3</sup> /d

The Henry's constant for ethylbenzene at 20 °C is  $8.43 \times 10^{-3}$  atm m<sup>3</sup>/mol ( $H_c = 0.351$ ) and the octanol/water partition coefficient is 1349 (Metcalf and Eddy, 1991).

The biodegradation constant has been estimated to be  $0.23 \text{ m}^3/\text{g VSS d}$  (Namkung and Rittmann, 1987).

Substituting these values into Equation B4 gives:

$$S = \left( \frac{870000}{870000 + 1.7 \times 10^6 + 9.2 \times 10^7 + 1.2 \times 10^4} \right) (0.018) \quad (\text{B5})$$

Solving for  $S$  gives  $1.66 \times 10^{-4} \text{ g/m}^3$  ( $0.166 \text{ } \mu\text{g/L}$ ) for the effluent concentration of ethylbenzene. The amount of ethylbenzene lost to volatilization, biodegradation, and sorption can be calculated by substituting  $S$  back into the equations for  $R_{\text{VOL}}$ ,  $R_{\text{BIO}}$ , and  $R_{\text{SOR}}$  given in Chapter 2. The results are shown in Table B2 below.

**Table B2** Removal of Ethylbenzene by Volatilization, Biodegradation, and Sorption.

Removal Mechanism	Ethylbenzene Removal (g/d)	Percent Lost
Volatilization	285.5	1.82
Biodegradation	15228.5	97.24
Sorption	1.9	0.01
Total	15515.9	99.07

Note: The amount of ethylbenzene present in the influent is  $(870,000 \text{ m}^3/\text{d})(0.018 \text{ g/m}^3)$  or  $15660 \text{ g/d}$ .

## APPENDIX C

### MASS BALANCE GENERATED BY ENVIROCAD FOR EXAMPLE PROCESS

#### STREAM REPORT

Stream Name	S-111	S-114	S-112	S-115	S-113
Source	CL-102	M-102	CL-102	M-102	CL-102
Destination	OUTPUT	OUTPUT	OUTPUT	M-101	M-102

#### Stream Properties

Activity U/ml	0	0	0	0	0
Temp deg C	25	25	25	25	25
Pressure bar	1	1	1	1	1

#### Environmental Stream Properties

TOC mgC/l	529495.2	17689	39.5	10000	10000
COD mgO/l	1827605	65965.4	141.4	20000	20000
ThOD mgO/l	1827605	65965.4	141.4	30000	30000
BODu mgO/l	292955.3	60654.5	95.1	40000	40000
BOD5 mgO/l	248916.1	44833.1	71.9	50000	50000
TKN mgN/l	0	4129.1	6	60000	60000
NH3 mgN/l	0	4129.1	6	70000	70000
NO3/NO2 mgN/l	0	0	0	80000	80000
TP mgP/l	0	724.4	1	90000	90000
TS mgSlds/l	0	36220.5	52.5	100000	100000
TSS mgSlds/l	0	36220.5	52.5	140000	140000
VSS mgSlds/l	0	32598.4	47.2	150000	150000
DVSS mgSlds/l	0	32598.4	47.2	160000	160000

Stream Name	S-111	S-114	S-112	S-115	S-113
Source	CL-102	M-102	CL-102	M-102	CL-102
Destination	OUTPUT	OUTPUT	OUTPUT	M-101	M-102
Daily Demands					
TOC kgO/d	1.5	1367.9	744	773.3	1546.6
COD kgO/d	5.3	5101.2	2660.3	1546.6	3093.3
ThOD kgO/d	5.3	5101.2	2660.3	2319.9	4639.9
BODu kgO/d	0.9	4690.5	1789.5	3093.3	6186.5
BOD5 kgO/d	0.7	3467	1352.7	3866.6	7733.1
TKN kgN/d	0	319.3	112.6	4639.9	9279.8
NH3 kgN/d	0	319.3	112.6	5413.2	10826.4
NO3/NO2 kgN/d	0	0	0	6186.5	12373
TP kgP/d	0	56	19.8	6959.8	13919.7
TS kgSlds/d	0	2801	987.7	7733.1	15466.3
TSS kgSlds/d	0	2801	987.7	10826.4	21652.8
VSS kgSlds/d	0	2520.9	888.9	11599.7	23199.4
DVSS kgSlds/d	0	2520.9	888.9	12373	24746.1
Component Flowrates (kg/h averaged)					
Ethylbenzene	0.0372	0.0236	5.9705	0.0236	0.0472
Oxygen	0	0	0	0	0
Water	0	3098.738	783968.8	3098.74	6197.476
Benzene	0.0163	0.0089	2.2564	0.0089	0.0178
Tetrachloroeth	0.0187	0.0115	2.9096	0.0115	0.023
Dichloroethane	0.0156	0.0076	1.9194	0.0076	0.0152
1,1,1-TriChEth	0.0364	0.0213	5.3852	0.0213	0.0426
Toluene	0.004	0.0024	0.604	0.0024	0.0048
Glucose	0	0.0055	1.38	0.0055	0.0109
Phenol	0.0007	0.0041	1.0475	0.0041	0.0083
DeadBiomass	0	12.1782	4.2982	12.1782	24.3564
Biomass	0	116.7076	41.1909	116.708	233.4152
Carb. Dioxide	0	0	0	0	0
TOTAL	0.1289	3227.709	784035.7	3227.71	6455.418

Stream Name	S-107	S-109	S-110	S-104	S-105
Source	M-101	AEB-101	AEB-101	CL-101	CL-101
Destination	AEB-101	OUTPUT	CL-102	OUTPUT	M-101

## Stream Properties

Activity U/ml	0	0	0	0	0
Temp deg C	25	25	25	25	25
Pressure bar	1	1	1	1	1

## Environmental Stream Properties

TOC mgC/l	10000	631.4	10000	594109	10000
COD mgO/l	20000	2181.1	20000	2023210	20000
ThOD mgO/l	30000	2181.1	30000	2023210	30000
BODu mgO/l	40000	331	40000	538434	40000
BOD5 mgO/l	50000	288.7	50000	410654	50000
TKN mgN/l	60000	0	60000	0	60000
NH3 mgN/l	70000	0	70000	0	70000
NO3/NO2 mgN/l	80000	0	80000	0	80000
TP mgP/l	90000	0	90000	0	90000
TS mgSlds/l	100000	0	100000	0	100000
TSS mgSlds/l	140000	0	140000	0	140000
VSS mgSlds/l	150000	0	150000	0	150000
DVSS mgSlds/l	160000	0	160000	0	160000

## Daily Demands

TOC kgO/d	189742.5	701.5	189714.4	50.2	188969.2
COD kgO/d	379485	2423.2	379428.7	170.8	377938.4
ThOD kgO/d	569227.5	2423.2	569143.1	170.8	566907.6
BODu kgO/d	758970	367.8	758857.4	45.5	755876.8
BOD5 kgO/d	948712.5	320.8	948571.8	34.7	944845.9
TKN kgN/d	1138455	0	1138286	0	1133815
NH3 kgN/d	1328198	0	1328001	0	1322784
NO3/NO2 kgN/d	1517940	0	1517715	0	1511754
TP kgP/d	1707683	0	1707429	0	1700723
TS kgSlds/d	1897425	0	1897144	0	1889692
TSS kgSlds/d	2656395	0	2656001	0	2645569
VSS kgSlds/d	2846138	0	2845715	0	2834538
DVSS kgSlds/d	3035880	0	3035430	0	3023507



Stream Name	S-107	S-109	S-110	S-104	S-105
Source	M-101	AEB-101	AEB-101	CL-101	CL-101
Destination	AEB-101	OUTPUT	CL-102	OUTPUT	M-101

Component Flowrates (kg/h averaged)

Ethylbenzene	44.2052	17.3571	6.0549	0.7508	44.1816
Oxygen	0	0	0	0	0
Water	790098.7	0	790166.3	0	787000
Benzene	39.1649	7.309	2.2906	0.7741	39.156
Tetrachloroeth	24.5412	9.1856	2.9513	0.4314	24.5297
Dichloroethane	19.5352	6.1732	1.9502	0.4331	19.5277
1,1,1-TriChEth	34.3319	17.5303	5.4641	0.6324	34.3106
Toluene	24.5178	1.8326	0.6128	0.4445	24.5155
Glucose	70.0055	0	1.3909	0	70
Phenol	49.9099	0.0076	1.0565	0.0854	49.9058
DeadBiomass	12.1782	0	28.6545	0	0
Biomass	216.7076	0	274.6061	0	100
Carb. Dioxide	0	83.1565	0	0	0
 TOTAL	 790633.8	 142.5519	 790491.3	 3.5517	 787406.1

Stream Name	S-101	S-102	S-103
Source	INPUT	EQ-101	EQ-101
Destination	EQ-101	OUTPUT	CL-101

## Stream Properties

Activity U/ml	0	0	0
Temp deg C	25	25	25
Pressure bar	1	1	1

## Environmental Stream Properties

TOC mgC/l	289.7	593814.6	289.7
COD mgO/l	904.4	2022518	904.4
ThOD mgO/l	904.4	2022518	904.4
BODu mgO/l	394.3	539078.6	394.3
BOD5 mgO/l	336.1	411280.1	336.1
TKN mgN/l	14.5	0	14.5
NH3 mgN/l	14.5	0	14.5
NO3/NO2 mgN/l	0	0	0
TP mgP/l	2.5	0	2.5
TS mgSlds/l	127	0	127
TSS mgSlds/l	127	0	127
VSS mgSlds/l	114.3	0	114.3
DVSS mgSlds/l	114.3	0	114.3

## Daily Demands

TOC kgO/d	5473.6	4.5	5473.6
COD kgO/d	17090.1	15.5	17090.1
ThOD kgO/d	17090.1	15.5	17090.1
BODu kgO/d	7451.7	4.1	7451.7
BOD5 kgO/d	6351.5	3.1	6351.5
TKN kgN/d	273.6	0	273.6
NH3 kgN/d	273.6	0	273.6
NO3/NO2 kgN/d	0	0	0
TP kgP/d	48	0	48
TS kgSlds/d	2400	0	2400
TSS kgSlds/d	2400	0	2400
VSS kgSlds/d	2160	0	2160
DVSS kgSlds/d	2160	0	2160

Stream Name	S-101	S-102	S-103
Source	INPUT	EQ-101	EQ-101
Destination	EQ-101	OUTPUT	CL-101

Component Flowrates (kg/h averaged)

Ethylbenzene	45	0.0676	44.9324
Oxygen	0	0	0
Water	787000	0	787000
Benzene	40	0.0699	39.9301
Tetrachloroeth	25	0.0389	24.9611
Dichloroethane	20	0.0392	19.9608
1,1,1-TriChEth	35	0.057	34.943
Toluene	25	0.0401	24.9599
Glucose	70	0	70
Phenol	50	0.0089	49.9911
DeadBiomass	0	0	0
Biomass	100	0	100
Carb. Dioxide	0	0	0

TOTAL	787410	0.3216	787409.7
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Overall Material Balance (kg/h averaged)

COMPONENT	IN	OUT	(OUT-IN)
Ethylbenzene	45	24.20676	-20.7932
Oxygen	0	0	0
Water	787000	787067.5	67.51301
Benzene	40	10.43476	-29.5652
Tetrachloroeth	25	12.59576	-12.4042
Dichloroethane	20	8.588213	-11.4118
1,1,1-TriChEth	35	23.66256	-11.3374
Toluene	25	2.927532	-22.0725
Glucose	70	1.385423	-68.6146
Phenol	50	1.154228	-48.8458
DeadBiomass	0	16.47636	16.47636
Biomass	100	157.8985	57.89851
Carb. Dioxide	0	83.15645	83.15645
TOTAL	787410	787410	-0.00044

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